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# Final Report for Research Conducted Under MPO B590872 between Lawrence Livermore National Laboratory and Lawrence Berkeley National Laboratory

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## In Situ Transmission Electron Microscopy and X-ray Spectroscopy for the Study of Advanced Materials for Energy Storage

(10-LW-045, LLNL PI: Jonathan Lee)

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## Introduction

The research conducted under MPO B590872 was divided into three tasks:

- (1) Conduct In situ TEM measurements of the evolution in electrode structure as a function of charge/discharge cycling
- (2) Assist with complementary in situ x-ray spectroscopy studies of electrode materials
- (3) Generate a final report

This document accounts for task (3) and our progress regarding tasks (1) and (2) is described within the following sections:

## In Situ TEM Studies

In situ TEM offers an unparalleled combination of high spatial and temporal resolution for investigating changes in the geometrical structure of materials under operating conditions. As such, it represents a powerful means of studying the structural evolution of rechargeable lithium ion battery (LIB) electrodes during charge-discharge cycling (i.e. lithium intercalation and removal), which holds crucial information for understanding the underlying mechanisms of charge storage and electrode degradation. All in situ TEM studies carried out under MPO B590872 were directed towards the investigation of advanced anode materials for LIBs, specifically tin (Sn) nanocrystals embedded in graphitic matrices, which were provided to our experimental team by Dr. Jonathan Lee (principle investigator of project 10-LW-045).

In order to study the effects of charge-discharge cycling on the Sn/graphite electrodes via in situ TEM, it was our aim to distinguish between the Sn nanomaterials and the graphitic matrix during imaging, since this would allow us to follow structural evolution of several components of the electrodes: (i) the Sn nanocrystals themselves, (ii) the interface between the nanocrystals and the graphitic matrix, including any solid electrolyte interphase (SEI) layer, and (iii) the graphitic matrix. Characterizing the evolution in these components holds the potentially ground-breaking information regarding how the electrodes intercalate/remove Li ions, how the SEI layer forms and how this affects Li intercalation/removal and how the graphitic matrix accommodates the large volumetric expansion expected for the Sn during intercalation, thereby improving the cyclability/lifetime of the electrode.

Our initial studies were aimed at establishing a baseline for subsequent TEM measurements of the Sn/graphite anodes *in operando*, via imaging the electrode materials (1) ex situ and (2) within a liquid cell without an applied bias. While successful, these experiments revealed important limitations in the structure of the electrode materials provided by Dr. Lee for use with the existing configuration of the in situ cell (originally designed for probing electrochemically induced/controlled mineralization) that would (i) prohibit electrochemical control over the system and (ii) prevent data collection with the required spatial resolution to gain new insight into the behavior of the Sn/graphite anodes. As a result, our research efforts were redirected towards tailoring the cell design and sample preparation to address these limitations. We were extremely successful in this regard and a list of the issues encountered and the means by which they were solved are listed below:

### (1) Excessive bowing of the cell windows

Our preliminary *ex situ* measurements (figure 1a) clearly demonstrated the capability to distinguish between the Sn nanocrystals and the graphitic matrix with TEM and even resolve lattice fringes in the nanomaterials. These results were encouraging because they suggested that one should be able to resolve the Sn nanomaterials from the graphitic matrix within an *in situ* cell, even accounting for the loss of spatial resolution expected when imaging through a liquid environment. Unfortunately, subsequent *in situ* measurements for the Sn/graphite electrodes within Li electrolyte revealed a significant problem with the cell design: the silicon nitride windows of the *in situ* cells were subject to a substantial amount of bowing across their width.

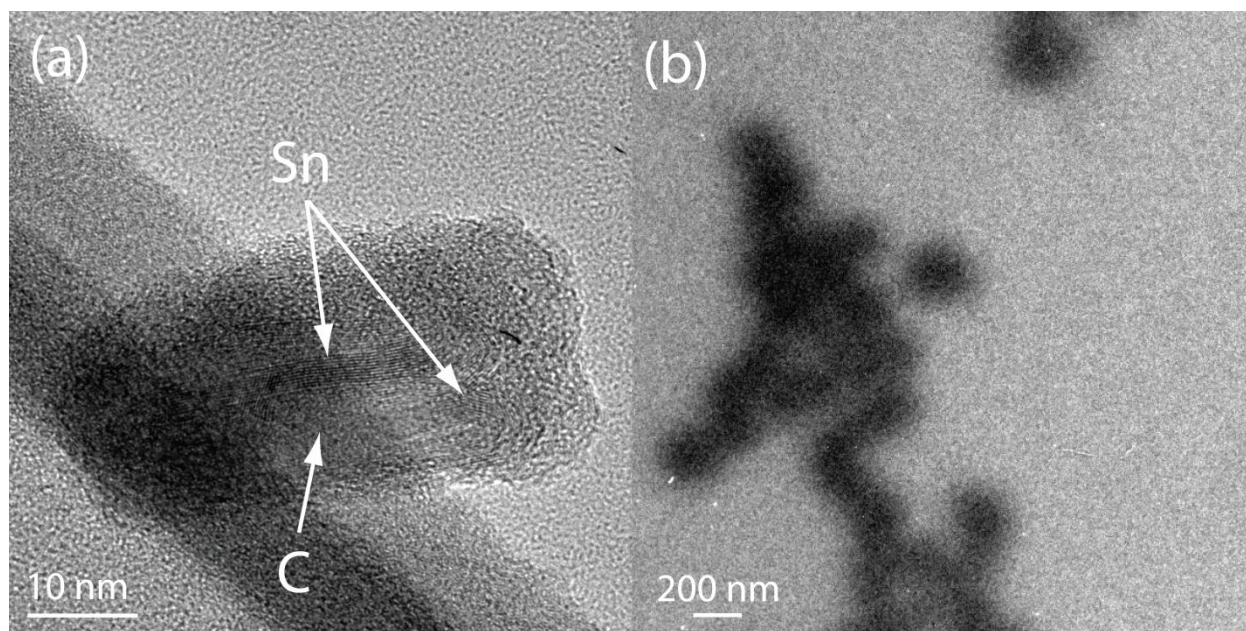


Figure 1: TEM images recorded under **(a)** *ex situ* and **(b)** *in situ* conditions for the Sn/graphite anode materials. The lattice fringes observed in the *ex situ* images arise from the Sn nanocrystals.

Bowing outwards resulted in electrolyte thicknesses in excess of 1  $\mu\text{m}$ , while bowing inwards resulted in touching of the windows or almost complete exclusion of electrolyte. Significantly, both conditions are extremely undesirable for imaging the electrode materials during charge/discharge cycling. The thick electrolyte layers associated with outward bowing of the windows resulted in considerable attenuation and scattering of the electron beam and, by extension, an inability to achieve the necessary spatial resolution to distinguish between the Sn nanoparticles and the graphitic matrix. In fact, the attenuation/scattering of the incident beam was so great that we were limited to resolving only the overall Sn/graphite composite (figure 1b). Inward bowing of the windows was a far less prevalent occurrence, but was equally problematic because the exclusion of electrolyte in the vicinity of the Sn/graphite electrode would cause a discontinuity in the circuit and prevent the system from operating as a battery. To further exacerbate the problem, the degree of window flex led to a higher than desired frequency of window cracking during assembly, which rendered many cells unusable prior to

measurement and raised concern regarding the risk of failure of unbroken cells in the high vacuum environment of the TEM.

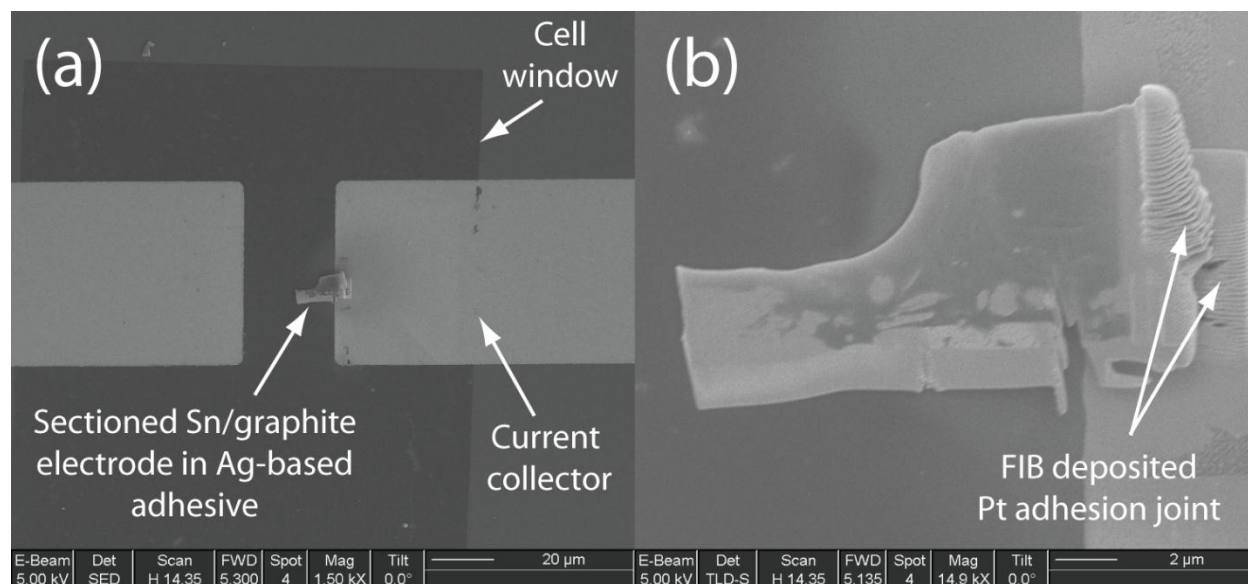
The cause of the window flexibility was identified as the combination of their large size and limited thickness ( $\leq 100$  nm). Increasing the window thickness to provide greater mechanical strength was not a viable solution to the problem because it would lead to an increasing in attenuation and scattering by the windows. Therefore, we redesigned the size and geometry of the window membranes to mitigate the excessive degree of bowing. The upper window in the original cell design was significantly oversized in order to facilitate use of EDS during experiments, under the assumption that the *in situ* stage would have a limited capacity to tilt given its relatively large height in the pole piece gap. In fact the stage has a tilt range of  $\pm 20^\circ$  in the microscopes used for experiments, allowing for EDS use with much smaller windows. Furthermore, the EDS capability is of secondary importance for the *in situ* TEM investigation of electrical energy storage materials - the ability to conduct high resolution imaging with a higher fidelity in cell construction should take precedence over the potential capability for chemical spectroscopy. With an updated window geometry and reduced window size, we anticipated a maximum flex of 50% at the center of the window, which corresponds to a nominal cell/electrolyte thickness of 500nm. In practice, we were able to achieve the sub-micron electrolyte thicknesses required for high resolution imaging of the LIB electrodes.

**(2) A: Traditional approaches for contact between anodes and current collector were unsuccessful, and B: conductive sealants used as an alternative were too thick to allow imaging**

In many commercial batteries and cells used for research applications, compression is sufficient to yield contact between the electrode and current collector. Unfortunately, this approach was unsuccessful during assembly of the original *in situ* cells employed for study of the Sn/graphite electrodes - the Sn/graphite composites could move within the liquid cells, thereby indicating that they did not have good electrical contact to the current collector (a metal pad) and the vias used to transport charge to and from the working electrode from outside of the cell. As a consequence, it was necessary to develop a means of attaching the working electrodes to the current collector, while ensuring that the electrochemical performance of the electrode was not affected and there was no increase in the sample thickness that would impact the spatial resolution of the *in situ* TEM measurement.

To address this problem, we implemented a technically challenging, but extremely reliable, approach to sample preparation. The Sn/graphite electrodes were encased in a conductive, carbon- or Ag-based, adhesive, which was then sectioned out via focused ion beam (FIB) to leave a small, thin section containing the electrode. This approach did not significantly affect the composition of the electrode but provided much more facile handling and manipulation of the material than the pure Sn/graphite powder, which tended to segregate during use. While within the FIB device, the sample was then transferred to a lower wafer of an *in situ* cell and precisely positioned on the current collector using a micromanipulator (figure 2). The FIB was used to detach the sample from the micromanipulator and deposit platinum across the joint between the sample and the current collector. This joint was sufficient to hold the sample rigidly in place and provide a robust electrical contact to the current collector (figure 2). The success of this approach is reflected in the scanning TEM measurements displayed in figure 3,

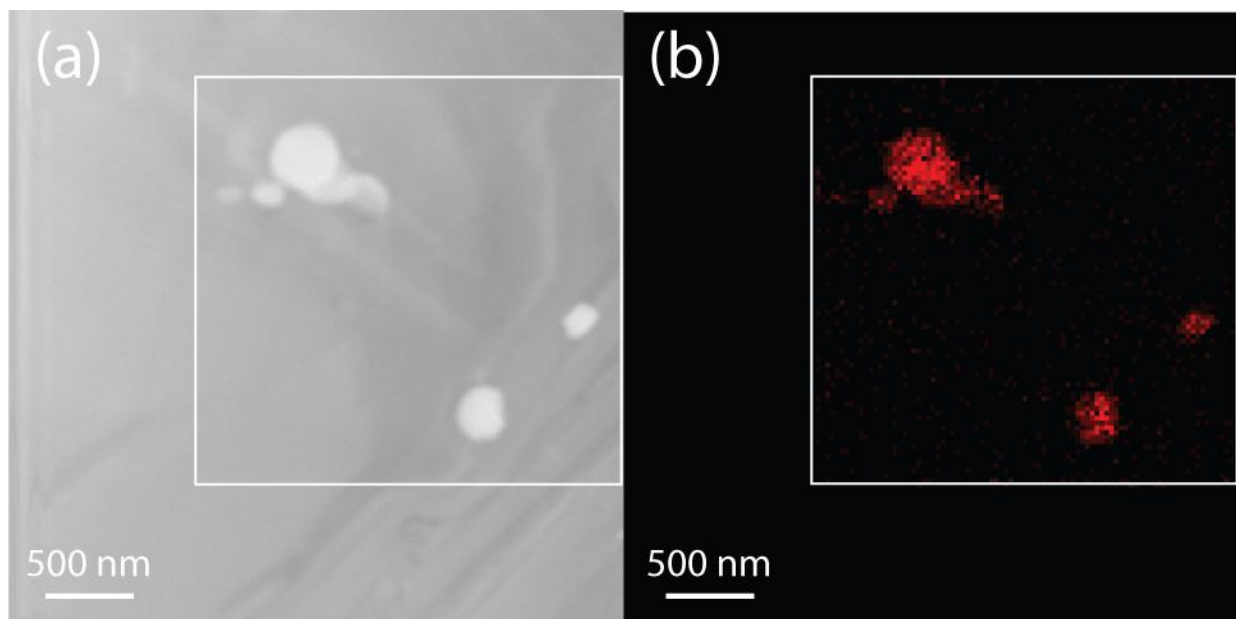
which clearly allow one to distinguish between the Sn and the surrounding graphitic matrix and also the carbon-based epoxy and Pt adhesion layer.



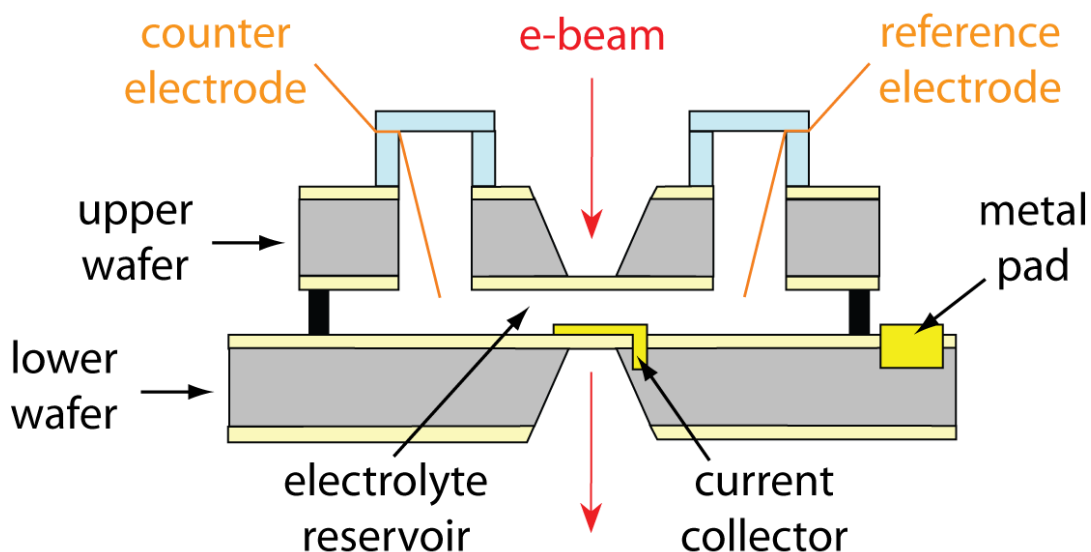
**Figure 2:** Scanning electron micrographs of a section of Sn/graphite electrode incased in Ag-based epoxy and mounted on the lower wafer of an in situ TEM cell. The micrograph displayed in (a) demonstrates the precision with which the electrode material is positioned within the cell – the sample is within the viewable region of the cell (above the window) and overlaps the current collector. The higher resolution micrograph presented in (b) enables observation of the FIB-deposited Pt layer used to secure the electrode in place and provide robust electrical contact between the electrode and the current collector.

### (3) The electrode configuration was non-optimal

Although the electrode configuration within the existing cell was viable under ideal conditions, it had significant shortcomings that required addressing for more robust and consistent performance in battery research applications. First, electrical contact to the current collector was often unreliable in parts produced both at LLNL and LBNL, which resulted from unreasonable requirements of the microfabrication process use to prepare the cell parts. The cell design required the path of electrical conductivity to run through the Si wafer of the lower window, between the current collector inside the cell and a metal pad on the outside (figure 4). This configuration required the precise deposition of ultra-thin metal layers on micron-scale features and numerous parts were found to be defective, either due to misalignment of the film and vias or discontinuities in the thin films themselves. Second, the counter and reference electrodes were incorporated into the cells through apertures used for the introduction of electrolyte (figure 4) and their presence led to problems in sealing these apertures during the final gluing step. As a consequence, it was not uncommon for electrolyte to either wick out of the apertures or evaporate, thereby leaving one or both of the wires not submerged in the liquid and precluding electrochemical control of the cell.



**Figure 3:** (a) Scanning TEM high angle annular dark field image of an Sn/graphite electrode encased in Ag-epoxy and attached to the lower window of an in situ cell and (b) the associated Z-contrast image to enhance the signal from Sn, which allows the nanocrystals to be readily resolved.

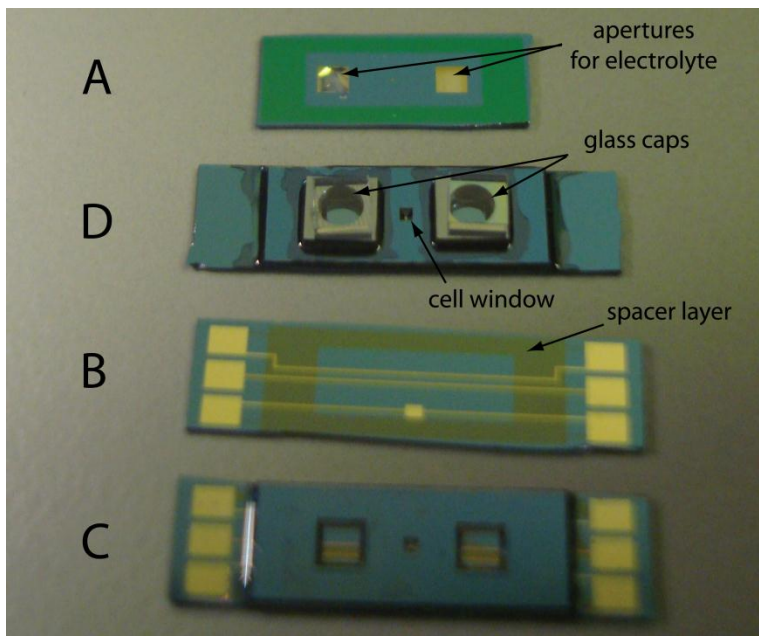


**Figure 4:** Schematic of the original design for the in situ TEM cell. In principle, the current between the metal pad and current collector is passed through the Si wafer (grey) but the contacts frequently failed due to discontinuities in the metal or misalignment of the deposited metal films

To address these problems we completely redesigned the lower part of the cell to facilitate more reliable electrical contact and sealing of the cell. As illustrated in figure 5, our new cell design has all three electrodes patterned on the silicon nitride membrane of the lower cell component. This avoids the need for multiple junctions between materials in the electrical conduction pathway, providing a continuous electrode from a point on the chip external to the fluid volume to the imaging window. This



new design also eliminates the need for insertion of wires into the solution reservoirs, and leads to much better sealing of the cell in the final gluing step. Moreover, one can readily change the metals used for the three electrodes/current collectors, which makes the design extremely versatile for the study of LIB material systems in a wide variety of potential regimes.



**Figure 5:** A photograph displaying the in situ cell components and various stages of these components during assembly. **A** is the upper wafer, which contains the two apertures for filling the cell with electrolyte. **B** shows the redesigned lower wafer that has all three electrodes/current collectors on its surface – note the large pads outside of the spacer layer to enable electrical contact. **C** has the upper and lower wafers sealed together with the apertures on the upper wafer open to allow filling with electrolyte and **D** shows the cell with these apertures sealed by glass caps. Note that the original cell design required passing the counter and reference electrodes into the apertures under these glass caps – this unseated the caps and frequently led to problems when attempting to seal the cell with epoxy.

#### (4) Cell deformation/damage due to sealant creep

The procedure used for cell assembly was such that an uneven pressure was applied across the area of the cell, occasionally resulting in epoxy/sealant creeping into the cell and/or the windows breaking from the stress. The epoxy wicking into the cell had two known detrimental effects: (i) it sometimes crept in between the windows or otherwise closed off the connection between the two reservoirs, preventing or hindering fluid from filling the gap between the two membranes and (ii) any slight swelling or bubble formation during cure of the epoxy pushed the upper and lower components of the cell apart, which resulted in an electrolyte layer thicker than the required value.

To address the problem of sealant creep into the cell, our team adapted a method of assembly reported in the literature by other leaders in the field of in situ TEM (specifically Prof. Francis Ross and co-workers), which yielded more reliable cell production. More specifically, we implemented a jig during cell assembly that provides even pressure across the cell to minimize the possibility of sealant wicking between the upper and lower components via capillary action. The result was a higher throughput of cell production, combined with fluid layer thicknesses suitable for in situ measurements of the Sn/graphite electrodes.

### Concluding Remarks

The Sn/graphite electrodes provided for this study presented far greater experimental challenges than the majority of systems previously studied with in situ TEM and fell beyond the limits of existing cell designs, which had previously been employed with great success for studies of electrochemically induced mineralization. It is important to note that, in part, these challenges arose due to a thicker than anticipated graphite layer on the Sn nanocrystals, which placed greater restrictions on the geometry and configuration of the cell to enable high resolution imaging. Significantly, we were able to address all of the limitations of the original cell design and to establish new protocols for sample preparation to provide a unique and robust experimental arrangement for the investigation of the Sn/graphite anodes or, indeed, any other candidate materials for use in LIBs. The development of the new cell and sample preparation protocols was a multistep process that required extensive design and research (including establishing new procedures for microfabrication of the cell parts or FIB machining and bonding of the anode samples and exploring the most appropriate adhesives for encasing the electrodes) and, as such, it was extremely time intensive process. Dr. Lee was informed of the experimental challenges and fully supportive of our approach to the problem. In addition, he was regularly updated of our progress on at least a monthly basis. At the time of writing, we are anticipating application of the new cell parts and modified Sn/graphite samples in in situ TEM measurements that will yield far better resolution and success than the in situ studies conducted earlier in the project.

### In Situ X-ray Spectroscopy Studies

In addition to his work relating to the in situ TEM measurements, Michael Nielsen played an important supporting role to the in situ spectroscopy studies led by PI Jonathan Lee. He assisted in sample preparation and data collection during a series of four experimental beamtimes (on beamlines 4.0.3, 7.0 and 8.0 at the Advanced Light Source, LBNL) and in the subsequent analysis of this data. As a result of his research in this area of the project, Michael was a co-author on a paper published in a peer-reviewed scientific journal:

Worsley M.A., Olsen T.Y., Lee J.R.I., Willey T.M., **Nielsen M.H.**, Roberts S.K., Pauzauskie P.J., Biener J., Satcher Jr. J.H., Baumann T.F., “High Surface Area,  $sp^2$ -crosslinked 3D Graphene Monoliths” *Journal of Physical Chemistry Letters*, 2011, **2**, 921